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Effects of Hydrostatic Pressure and of Jahn-Teller Distortions on the Magnetic Properties of $RbFeF_3$†

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The first-order transitions at $T_1=40°K$ and $T_2=87°K$ in $RbFeF_3$ have been measured as a function of hydrostatic pressure and applied magnetic field. It was not possible to observe the $T_N=102°K$ transition with a magnetic-susceptibility measurement. It was found that $(\Delta T_1/\Delta H_a)_p=0.35°/\mathrm{kOe}$, $(\Delta T_2/\Delta H_a)_p=0.19°/\mathrm{kOe}$, $(\Delta T_1/\Delta P)_H=0.18°/\mathrm{kbar}$ and $(\Delta T_2/\Delta P)_H=-0.81°/\mathrm{kbar}$. These results correspond to latent heats of 0.006 and 0.04 cal/g at T_1 and T_2, respectively, and relative volume changes $\Delta V_1/V_1=1.5\times10^{-6}$, $\Delta V_2/V_2=-22\times10^{-6}$. It is pointed out that a Jahn-Teller distortion to tetragonal $(c/a>1)$ symmetry in the interval $T_2<T<T_N$ introduces a strong magnetoelastic coupling. This causes the heavy twinning that has been observed below T_N, and the resulting twinned structure is retained in the entire temperature interval $0<T<T_N$. In the temperature interval $T_1<T<T_2$, Rb^+-F^- interactions induce distortions to orthorhombic or tetragonal symmetries that are superimposed on the Jahn-Teller distortion. The orthorhombic distortion is cooperative across twin boundaries caused by the Jahn-Teller distortion and also permits spin canting, which introduces a ferromagnetic component below T_2. It is shown how the interplay of these distortions plus strong magnetoelastic coupling can explain the appearance of two sets of Mössbauer peaks below T_2 and results in macroscopic ferromagnetic components having cubic symmetry even though the microscopic crystallographic symmetry is "orthorhombic" $(T_1<T<T_2)$. The Jahn-Teller distortion changes to rhombohedral $(\alpha<60°)$ for $T<T_1$; in combination with the existing orthorhombic structure, this produces monoclinic symmetry on a microscopic scale. Nevertheless, it is shown that the macroscopic magnetization retains its cubic symmetry, that the easy magnetization direction changes from $\langle100\rangle$ to the $\langle110\rangle$, that the apparent moment increases, and that there may still be two sets of Mössbauer peaks.

I. INTRODUCTION

Above its Néel temperature $T_N=102°K$,[1] $RbFeF_3$ has the cubic perovskite structure, but it becomes tetragonal $(c/a>1)$ in the interval $T_2<T<T_N$.[2] It undergoes first-order transitions at $T_1=40°K$ and $T_2=87°K$; it exhibits weak ferromagnetism at all $T<87°K$.[3] In the interval $T_1<T<T_2$, the structure appears to be orthorhombic, and below T_1 it has lower symmetry, probably monoclinic.[2] The ferromagnetic moment has a preferred direction along the pseudocubic $\langle100\rangle$ axes in the interval $T_1<T<T_2$, along the pseudocubic $\langle110\rangle$ axes below T_1.[4] It is remarkable that these noncubic crystals exhibit a cubic macroscopic anisotropy of the weak ferromagnetism. A neutron-diffraction study on a polycrystalline sample shows the dominant magnetic

structure to be a simple type-G antiferromagnet for all $T < T_N$.[5] However, Mössbauer measurements below T_2 distinguish two types of iron sites, and this finding was claimed to be incompatible with a simple canting of the spins to produce the weak ferromagnetism.[1]

The transition temperatures T_1 and T_2 both vary with applied magnetic field H_a. Wertheim *et al.*[1] obtained a shift of T_2 to 95°K and of T_1 to 45°K in an $H_a = 14\,240$ Oe, corresponding to a $\Delta T_2/\Delta H_a = 0.56°/\text{kOe}$ and a $\Delta T_1/\Delta H_a = 0.35°/\text{kOe}$. Testardi *et al.*,[2] on the other hand, required a field of 4 kOe to achieve a $\Delta T_2 \approx 0.5°\text{K}$, corresponding to a $\Delta T_2/\Delta H_a \approx 0.125°\text{K}$. No discussion was given of the rather striking difference in the two results.

In this paper we report studies of the magnetic properties of $RbFeF_3$ in the vicinity of the first-order transformations as functions of both applied field and hydrostatic pressure. We also present a microscopic interpretation of the magnetic and crystallographic data.

II. EXPERIMENTAL

The powder sample used in these measurements was obtained by grinding a single crystal grown by O'Connor. The starting material was obtained from the reaction of high-purity RbF and $FeCl_2$ heated in a graphite crucible to 1000°C. RbCl was removed from the product by dissolving in water. Crystals were grown from the melt in a graphite crucible contained in a sealed nickel crucible, with provision for adding a small amount of NH_4HF_2. A sharp temperature gradient provided optimum growth conditions.

The measurements were performed on a vibrating-coil magnetometer used in conjunction with a helium-gas pressure-generating unit. This system permits the direct measurement of magnetic moment while freely varying applied field, temperature, and pressure.[6]

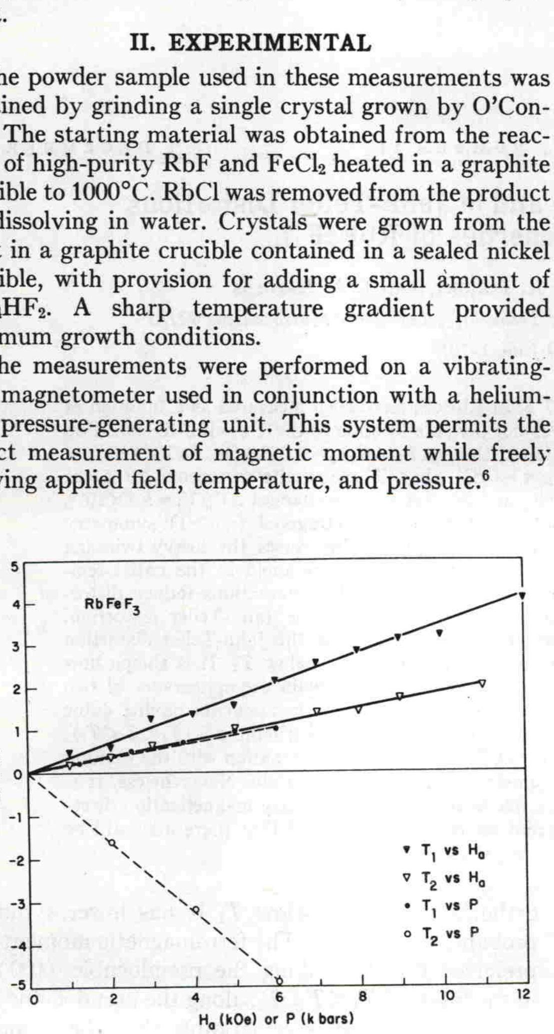

FIG. 1. Changes in the $RbFeF_3$ transition temperatures T_1 and T_2 as functions of applied magnetic field strength H_a or hydrostatic pressure P.

TABLE I. Parameters of the two first-order transitions in $RbFeF_3$.

T_i (°K)	$(\partial T_i/\partial H)_P$ (deg/kOe)	$(\partial T_i/\partial P)_H$ (deg/kbar)	L_i (cal/g)	$(\Delta V_i/V_i)$ ($\times 10^6$)
41	0.35	0.18	0.006	1.5
87	0.19	−0.81	0.04	−22

The magnetization-versus-temperature curve closely approximated that given by Wertheim *et al.*,[1] except that our measured saturation moment at 4.2°K was approximately 14.5 emu/g rather than the 16 emu/g they obtained. This 10% drop can be explained by the fact that our measurements were taken on a polycrystalline sample in fields up to $H_a = 12$ kOe, since the anisotropy investigations of Gyorgy *et al.*[4] indicate that at these applied fields the magnetization is limited to the easy-axis direction closest to the field. The magnetization curve is characterized by a pronounced step at T_1.

Investigation of the magnetization in the temperature range $90 \leq T \leq 120°\text{K}$ and in fields $1 < H_a \leq 10$ kOe at both atmospheric pressure and at 5 kbar showed no observable kink in the magnetization-versus-temperature curves in the vicinity of T_N. This accords with the results of Wertheim *et al.*[1] and supports their conclusion that lattice strains produced by crystallographic distortions accompanying short-range magnetic order give rise to a spatial variation of T_N.

Magnetic-moment measurements in the vicinity of the two first-order transitions showed that application of hydrostatic pressure, though shifting T_1 and T_2, induced no significant change in the magnitudes of the weak ferromagnetic components as a function of $(T_1 - T)$ or $(T_2 - T)$, where $T_1 \approx 41°\text{K}$ in our sample. The variations of T_1 and T_2 with pressure and applied field were found to be linear for pressures $1 < P < 6$ kbar and fields $1 < H_a < 12$ kOe. The results of several measurements are shown in Fig. 1. The resultant slopes are listed in Table I. We found a $\Delta T_1/\Delta H_a \approx 0.35°/\text{kOe}$, in good agreement with that implicit in the data of Wertheim *et al.*[1] The measured sharp increases in ferromagnetic moment $\Delta\sigma_1$ and $\Delta\sigma_2$ on cooling through the transitions at T_1 and T_2 were found to be 2.0 and 3.5 emu/g, respectively. The latter value differs significantly from the 5 emu/g obtained by Testardi *et al.*[2] Substitution of these values into the Clausius-Clapeyron equations

$$\left.\frac{\partial T}{\partial H_a}\right)_P = -\frac{\Delta\sigma_i}{L_i} T_i \quad \text{and} \quad \left.\frac{\partial T}{\partial P}\right)_{Ha} = \frac{\Delta V_i}{L_i} T_i \qquad (1)$$

permits determination of the latent heats L_i and volume changes ΔV_i associated with each of these transitions. These are also listed in Table I. The negative value of ΔV_2 indicates a volume expansion on cooling through the $T_2 = 87°\text{K}$ transition. The relative volume changes $\Delta V_i/V_i$ are seen to be quite small, probably falling